

NUCLEAR MAGNETIC RESONANCE IMAGING STUDIES OF ASPHALTENE PRECIPITATION IN AGED AND UNAGED ASPHALTS

Francis P. Miknis and Adam T. Pauli
Western Research Institute
365 N. 9th Street
Laramie, WY 82070-3380

Keywords: magnetic resonance imaging, asphalt, asphaltenes, aging

INTRODUCTION

Nuclear magnetic resonance (NMR) imaging is a powerful, relatively new technique that can be used for noninvasive chemical and physical characterization of local regions in the interior of intact samples. One of the more promising aspects of the technique is its ability to characterize chemical and physical processes noninvasively over time. Because of this ability and the optical opacity of asphalt systems, the potential of NMR imaging in the study of asphalts is being investigated [1]. The work reported here is an exploratory application of NMR imaging to study asphaltene precipitation in oxidatively aged asphalts. Although NMR imaging has been used mostly in medical applications, nonmedical applications are increasing and have recently been reviewed [2].

Historically, asphalts have been modeled as dispersions of associated molecules, referred to as asphaltenes, in an oily solvent phase referred to as maltenes. The asphaltenes are more aromatic and contain more heteroatoms than do the maltenes; therefore, their intermolecular interactions are generally more extensive. Consequently, asphaltenes are largely responsible for the internal structure of asphalts and tend to dominate many of the physical properties of asphalts [3]. The effectiveness by which asphaltenes are dispersed by the maltenes determines the compatibility of an asphalt. Compatible asphalts have smaller amounts of asphaltenes than incompatible asphalts. Thus, a measurement of the amount of asphaltenes in an asphalt is a measure of its compatibility.

The standard method to determine asphalt compatibility is the Heithaus test [4]. In this procedure, samples of asphalt are dissolved in an aromatic solvent, such as toluene, and titrated with an aliphatic solvent, such as n-heptane. The compatibility properties of an asphalt are then determined by measuring the onset of flocculation brought about by the addition of the titrating solvent to solutions of the dissolved asphalt at different concentrations. The Heithaus procedure is somewhat operator dependent. Recently, an automated Heithaus method has been developed to test neat asphalts, cross blended materials, and oxidatively aged asphalts that eliminates the operator dependency [5].

The compatibility of an asphalt is important for practical reasons because the degree of asphalt compatibility affects *inter alia* rutting propensities and oxidative age hardening. The effects of asphalt composition on these and other roadway failure mechanisms are currently being investigated at Western Research Institute under contract with the Federal Highway Administration. As part of that study, nuclear magnetic resonance (NMR) imaging methods are being explored to study asphaltene dispersion and aggregate behavior, and compatibility in oxidatively aged asphalts. Some results of this study are the subject of this paper.

EXPERIMENTAL

The asphalts studied are part of the Strategic Highway Research Program (SHRP) Core asphalts [6]. Their chemical properties have been characterized [7] and some are listed in Table 1. The asphalts were aged using a combination of thin film oven (TFO) and pressure aging vessel (PAV) aging [8]. NMRI measurements were made on asphalts AAB-1, AAD-1, AAK-1, AAM-1, and ABM-1 that were PAV aged for 12 hrs @ 100°C. Additional NMRI measurements were made on asphalts AAE and AAS-1 that were both PAV aged for 144 and 400 hrs at 60°C. In one set of experiments, asphalt

AAD-1 was aged using a combination of TFO aging only, and TFO aging followed by PAV aging. This produced a set of 4 samples consisting of unaged, TFO aged, and TFO followed by PAV aging for 4 and 12 hrs at 100°C.

Samples were prepared for NMRI imaging experiments in the following way: Aged and unaged asphalt samples were dissolved in toluene. To this mixture, isooctane was added to cause flocculation and asphaltene precipitation. The amount of isooctane needed to cause maximum flocculation was calculated from previous work on the development of an automated Heithaus method [5]. Two samples were prepared for each asphalt. In one case, the samples were stirred after the addition of the isooctane, and in the other case, the isooctane was added slowly to the asphalt-toluene solution to minimize mixing at the solvent interface. Images were acquired after the addition of the isooctane and for different times afterwards to observe settling of the asphaltenes.

NMR imaging experiments were carried out at a nominal proton resonance frequency of 200 MHz using a Chemagnetics/Otsuka Electronics microimaging probe. Samples for NMR imaging experiments were placed in 23 mm (OD) glass vials, which were then placed in 25 mm (OD) glass tubes. The tubes were inserted into the MRI probe and were positioned in the probe using O-rings such that the cross sections to be imaged were contained in the experimental field of view (FOV).

NMR images of asphaltene precipitation were made using the spin echo method. Images were acquired using a pulse delay of 1 s, a free induction decay size of 256 data points, 128 phase encodes, and a gradient strength of 34 G/cm. The echo time was varied from 40 to 80 ms. Eight slices, 1 mm thick and separated by 1 mm were obtained. The time required to obtain a set of images was about 35 minutes using these parameters.

RESULTS AND DISCUSSION

The effects of aging (oxidation) and stirring on asphaltene precipitation, as viewed with NMR imaging, are illustrated in Figure 1. In these images, and in the images in subsequent figures, only the 4th slice of an image set of 8 slices is shown. The 4th slice corresponds closely to the longitudinal cross section across the center of the sample vial. The times listed in Figure 1 are settling times and refer to the time elapsed between addition of isooctane and the time when the image was recorded. Also, in Figure 1 and in all other figures, the different contrasts represent regions of different molecular mobility. Thus, the lightest areas of contrast in Figure 1 are due to the hydrogens in molecules that have a fair degree of molecular mobility such as the dissolved asphalt, toluene and isooctane. The darker regions in the images are due to hydrogens in molecules having a greater degree of molecular association (hence less molecular mobility) such as the asphaltenes.

When isooctane was added to the unaged AAD-1 asphalt and the mixture stirred, the asphaltenes settled to the bottom of the vial in a normal fashion (Figure 1a). When isooctane was added to the sample of AAD-1 asphalt that was aged for 12 hrs at 100°C and the mixture stirred, the asphaltenes settled to the bottom of the vial also in a normal fashion (Figure 1b). However, when isooctane was added to the top of the aged AAD-1 asphalt/toluene solution without stirring, an additional layer of material formed at the isooctane-toluene/asphalt interface that appeared to have experienced different solvent interactions than did the asphaltenes. This is illustrated by the dark band in Figure 1c that formed at about the level of the original isooctane-toluene/asphalt interface and which appeared to be quite stable upon setting for some periods of time. As these are cross sectional images, the dark band is actually a layer at the interface.

The time evolution of the interface layer is shown in Figure 2a-d by the images taken at different settling times after addition of the isooctane. The first image (Figure 2a) shows the asphalt dissolved in toluene before addition of the isooctane. Figure 2b was taken after isooctane was added, unstirred to the sample vial, and before the asphaltenes could settle to the bottom. In this image a thin layer of additional

material, which also contains spherical globules, can already be seen forming at the solvent interface. After one day of undisturbed settling, (Figure 2c) the layer is becoming more prominent and additional globules can be seen forming near the interface layer. The precipitation of asphaltenes is also noted by the darker diffuse band developing below the interface (Figure 2b). After one week (168 hrs) of settling, the interface layer is still apparent and the asphaltenes can be seen settling to the bottom of the vial (Figure 2d). On other samples, the layer has been imaged for settling times of up to 648 hrs. A set of radial images, 1 mm thick and separated by 1mm, through the interface layer of Figure 2d is shown in Figure 3a-d. This set of images shows the inhomogeneity of the asphalt solution. The distribution of spherical globules in and near the interface is shown in Figure 3b and c.

The formation of the dark layer appears to be related to the degree of aging. In Figure 4a-d, the asphaltene layer is seen at the bottom of the vial in all images for a settling time of 1 week and no dark layer is visible in the unaged and mildly (TFO) aged samples (Figure 4a and b). However, the dark layer is present at the interface for the PAV aged samples (Figure 4c and d) and is most pronounced for the asphalt sample that was aged the longest.

The formation of the interface layer appears to depend also on the concentration of asphaltenes in the unaged asphalt. In addition to asphalt AAD-1, the layering was observed in asphalts AAB-1, AAK-1 and AAE. All of these asphalts have asphaltene concentrations of about 20% or greater (Table 1). The layering was not observed in asphalts AAM-1 and ABM-1, which have low asphaltene concentrations, nor was it observed in asphalt AAS-1, which has a high asphaltene concentration. The reasons for the anomalous behavior of asphalt AAS-1 are not known at present. Asphalts AAS-1 and AAE were both PAV aged at a lower temperature (60°C), but for longer periods of time (144 and 400 hrs). Both have high concentrations of asphaltenes, but only AAE demonstrated the effect. The effects of time and temperature on asphaltene precipitation are currently under study.

The chemical nature of the material near the isooctane-toluene/asphalt interface is not known. This layer could be due to asphaltenes that are becoming more rigid with time at the isooctane-toluene/asphalt interface. A more rigid system would have shorter relaxation times and would appear darker in the NMR images. The layer could also be due to oxidation of the maltenes, which are then attracted to the highly polar surface of the asphaltenes and form a distinct layer at the interface. Compositional factors such as the amounts of strong and weak acids, bases and neutrals probably also contribute to the extent of oxidation and the associated interactions. Other possibilities exist. Nevertheless, the layer of material at the interface appears to have properties that are different from the asphaltenes and the maltenes. For example, the dark layer appears to be a more rigid material than the asphaltene layer. If the sample is stirred with a spatula the dark layer breaks into pieces. An example is shown in Figure 5. The top two images show the breakup of the interface layer longitudinally across the solvent-asphaltene boundary. The bottom two images show the breakup of the interface layer radially across the solvent-asphaltene boundary. In both types of images, the rigid nature of the interface layer is apparent. This material will need to be characterized in the future to determine how it might affect asphalt compatibility.

SUMMARY

Applications of magnetic resonance imaging to study various aspects of asphalts are in their infancy. Consequently, a number of imaging methods and instrumental parameters need to be investigated to determine the feasibility of MRI to study asphalts. In this study, exploratory MRI measurements were made on the effects of aging on the flocculation and precipitation of asphaltenes from asphalt. NMR images were obtained on asphalts which were dissolved in toluene and titrated with isooctane to the point of maximum flocculation. When the titrant was added slowly to minimize mixing at the isooctane-asphalt/toluene interface, the images showed that a layer of material formed at the solvent interface which was different from the asphaltenes or the maltenes. The formation of this layer appeared to be dependent on asphaltene

concentration and degree of aging, i.e., the greater the asphaltene content and the degree of aging, the more prominent the layer. These observations suggest that NMR imaging might be used to assess the compatibility of aged asphalts and work is in progress along these lines.

DISCLAIMER

This document is disseminated under the sponsorship of the Department of Transportation in the interest of information exchange. The United States Government assumes no liability for its contents or use thereof.

The contents of this report reflect the views of WRI which is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or the policy of the Department of Transportation.

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand to the exclusion of others that may be suitable.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support of this work by the Federal Highway Administration under Contract No. DTFH61-92C-00170.

REFERENCES

1. Miknis, F. P.; Netzel, D. A., *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1996**, 41(4), 1327-1331.
2. Komoroski, R. A., *Anal. Chem.*, **1993**, 65, 1068A.
3. Boduszynski, M. M., in *Chemistry of Asphalts*, J. W. Bunger and N. C. Li, eds, *Advances in Chemistry Series*, **195**, Amer. Chem. Soc., Washington, DC, 1981, 119-135.
4. Heithaus J. J., *J. Inst. Petrol.*, **1960**, 48, 45-53.
5. Pauli, A. T., *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **1996**, 41(4), 1327-1331.
6. Cominsky, R. J.; Moulthrop, J. S.; Elmore, W. E.; Kennedy, T. W., *SHRP Materials Reference Library Asphalt Selection Process*; Report No. SHRP-IR-A-89-002; Strategic Highway Research Program, National Research Council, Washington, DC, 1989, 31 pp.
7. Branthaver, J. F., et al., SHRP-A-368, *Binder Characterization and Evaluation, Volume 2: Chemistry*, Strategic Highway Research Program, National Research Council, Washington, DC, 1993, 193 pp.
8. Petersen, J. C., et al., SHRP-A-370, *Binder Characterization and Evaluation, Volume 4: Test Methods*, Strategic Highway Research Program, National Research Council, Washington, DC, 1994, 479 pp.

Table 1. Summary of Chemical Properties of Selected Asphalts

Property	AAB-1	AAD-1	AAE	AAK-1	AAM-1	ABM-1	AAS-1
Asphalt Grade	AC-10	AR-4000	60/70	AC-30	AC-20	AR-4000	AC-20
Crude Source	WY Sour	Calif.	Lloyd- minster air blown	Boscan	West Tex. Intermed.	Calif. Valley	Arab Heavy
<u>Component Analysis, %</u>							
Asphaltenes	19.3	23.9	24.8	22.9	9.4	8.3	21.3
Polar Aromatics	38.3	41.3	30.5	41.8	50.3	52.4	34.1
Napthene Aromatics	33.4	25.1	31.6	30.0	41.9	29.6	39.7
Saturates	8.6	8.6	12.7	5.1	1.9	9.0	5.9
<u>Other Properties</u>							
Carbon Aromaticities	0.32	0.24	0.33	0.32	0.25	--	--
Hydrogen Aromaticities	0.071	0.068	0.087	0.068	0.065	--	--
H/C	1.55	1.59	1.45	1.46	1.55	1.43	1.43
Molecular Weight (in toluene)	840	700	--	860	1300	--	960

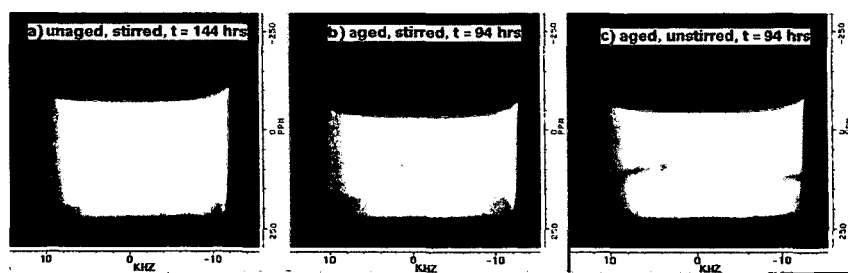


Figure 1. NMR images illustrating effects of aging and stirring on asphaltene precipitation. Times listed are settling times and refer to the time elapsed between addition of isooctane and the time when the image was recorded.

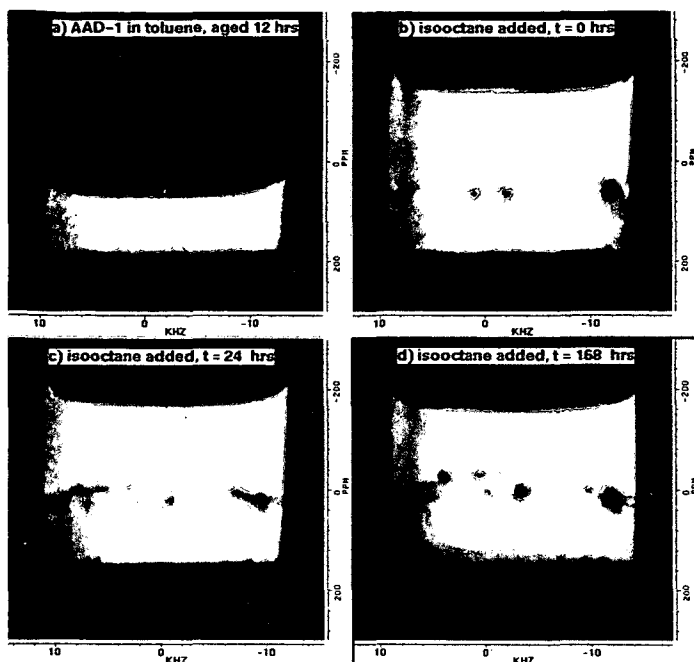


Figure 2. NMR images illustrating time evolution of interface layer in aged asphalt. Times listed are settling times.

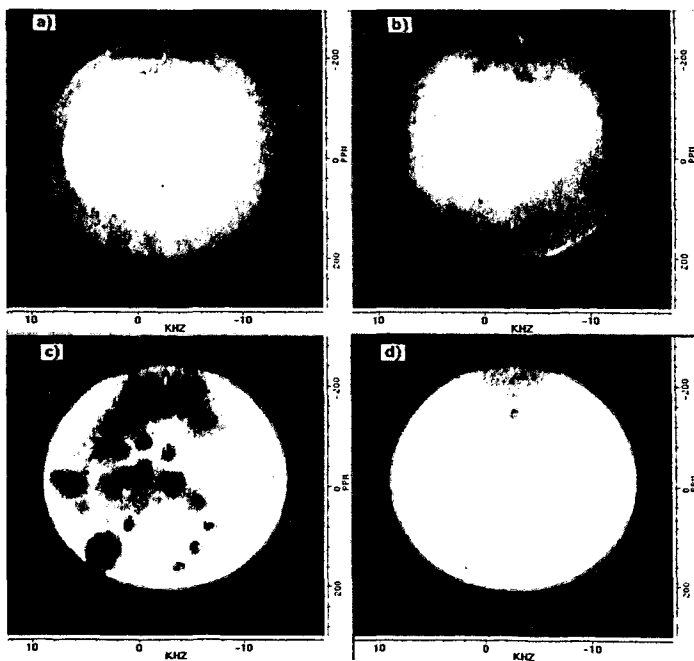


Figure 3. Radial NMR images at different depths illustrating spherical globules in the solvent interface layer.

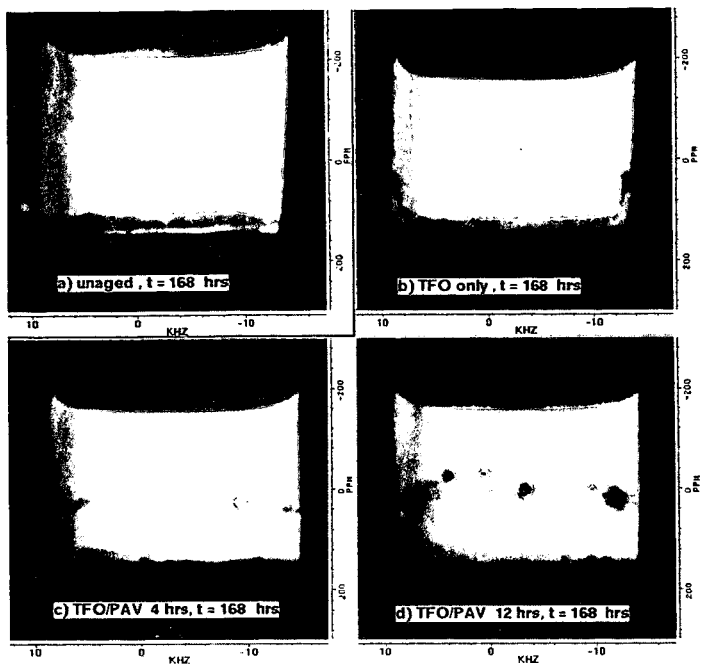


Figure 4. NMR images illustrating the effect of aging on asphaltene settling.

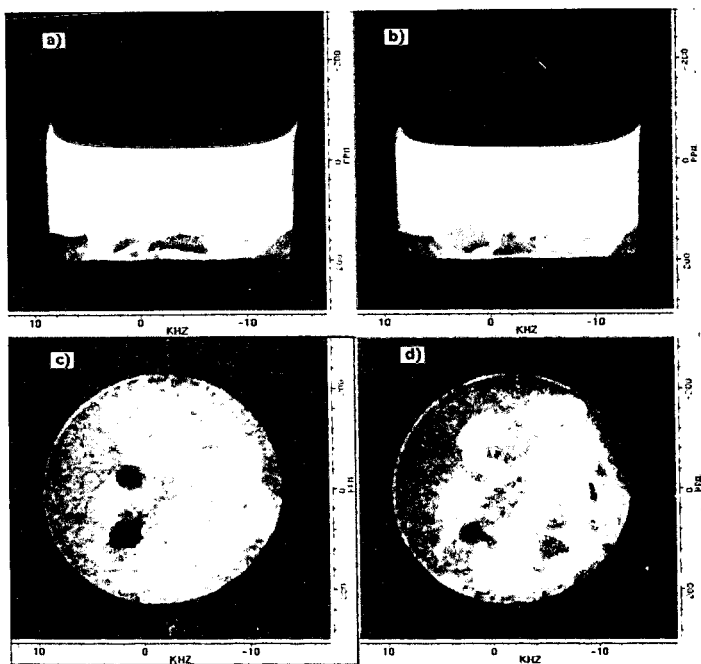


Figure 5. NMR images illustrating breakup of interface layer with stirring. a), b) Longitudinal cross-section images at different positions, c), d) Radial cross-section images at different positions.